

ARRHENIUS ACTIVATION ENERGIES OF THE REACTION OF LOW-RANK COAL CHARs AND STEAM

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Introduction

The chemical reaction between coal char and steam to produce synthesis gas, CO and H_2 , is well known. These products can be used directly as low-heating-value gas or as precursors for the catalytic synthesis of methanol and ammonia, oxo compounds, methane and petroleum substitutes. More recently, however, interest has centered on producing the gas for its hydrogen content. The hydrogen can be purified for use as a fuel.

The rate of the reaction involving char and steam is increased markedly by the use of catalysts, particularly alkali metal compounds (1-3). Potassium carbonate, which is commonly recognized as the best alkali catalyst for this reaction (4), was chosen as the catalyst to use in examining the gasification of chars prepared from Indian Head and Velva North Dakota lignites, and Wyodak Wyoming subbituminous coal. These three low-rank coals were converted to chars and then reacted with steam at 700°, 750° and 800°C both with and without K_2CO_3 catalyst. The course of the reaction was followed by thermogravimetric analysis (TGA). Sodium carbonate was also used to catalyze the Velva and Indian Head char-steam reactions. Sodium carbonate is a less expensive material than K_2CO_3 and, if shown to be an effective catalyst in place of K_2CO_3 , could reduce considerably the cost of the conversion process.

This paper reports the apparent Arrhenius energies of activation (E_a) and pre-exponential factors (A) for the steam gasification of the uncatalyzed and K_2CO_3 -catalyzed Velva, Indian Head, and Wyodak coal chars, and the Na_2CO_3 -catalyzed Velva and Indian Head coal chars.

Experimental

The three low-rank coals and their composition are shown in Table I. Table II shows the experiment matrix. Each coal was ground to 100 x 140 mesh and a portion of the ground coal was mixed intimately with 10 wt% dry K_2CO_3 or Na_2CO_3 for the catalyst tests. The coals in both the uncatalyzed and catalyzed form were devolatilized and then reacted with steam in a Du Pont 951 Thermo-gravimetric Analyzer (TGA) interfaced with a Du Pont 1090 Thermal Analyzer. The devolatilization removed the moisture and the volatile matter from the coal and produced the char containing the active fixed carbon for the steam-carbon reaction.

(a) Devolatilization.

Approximately 20 mg of uncatalyzed or catalyzed coal was loaded on the sample pan of the thermogravimetric analyzer. A flow of 275 mg/min Argon was passed through the reaction chamber during the devolatilization of the coal. The sample was heated at 100°C/min to one of three temperatures, 700°, 750°, or 800°C. After the target temperature was achieved, isothermal heating at that temperature was continued until at least 15 minutes total time had elapsed. The resulting char was held under flowing argon without cooling until the char-steam reaction was initiated.

(b) Char-Steam Reaction.

Steam was introduced through a side-arm of the quartz furnace tube at a rate of 1-6 mg/min. The argon flow was reduced to 100 mg/min during the steam reaction. As the reaction proceeded, the loss of weight was recorded at the rate of one data point every two seconds until the char reached constant weight. The rate parameter, k , was calculated from the data obtained and the energy of activation (E_a) was calculated from the plots of $\ln k$ versus $1/T$ for the three reaction temperatures.

Table I. Low-Rank Coal Composition.

	Indian Head	Velva	Wyodak
<u>Proximate Analysis (AR) wt%:</u>			
Moisture	36.62	38.8	30.99
Volatile Matter	26.07	25.3	30.43
Fixed Carbon	30.50	29.0	32.96
Ash	6.81	6.9	5.62
<u>Ultimate Analysis (MAF) wt%:</u>			
Carbon	70.4	70.4	73.7
Hydrogen	5.45	5.30	5.38
Nitrogen	1.40	1.40	1.22
Oxygen (by diff)	21.7	22.3	19.1
Sulfur	1.04	0.60	0.53
<u>Ash Analysis (wt% of ash):</u>			
SiO ₂	26.25	19.6	28.0
Al ₂ O ₃	10.73	12.7	15.0
Fe ₂ O ₃	14.03	5.8	4.30
TiO ₂	0.53	0.40	1.20
P ₂ O ₅	0.42	0.60	1.50
CaO	15.95	36.0	21.7
MgO	4.88	10.20	6.60
Na ₂ O	7.97	2.10	1.60

Table II. Reaction of Devolatilized Coal Char With and Without 10 wt% Catalyst.

Reaction Temp., °C Catalyst	700			750			800		
	None	K ₂ CO ₃	Na ₂ CO ₃	None	K ₂ CO ₃	Na ₂ CO ₃	None	K ₂ CO ₃	Na ₂ CO ₃
<u>Coal Reacted:</u>									
Indian Head	X	X	X	X	X	X	X	X	X
Velva	X	X	X	X	X	X	X	X	X
Wyodak	X	X		X	X		X	X	

Results and Discussion

Preliminary experiments were conducted to determine optimum operating parameters for the reaction on the TGA. It was determined that a catalyzed or uncatalyzed low rank coal sample size of ~20 mg produced a satisfactory quantity and quality of char when devolatilized according to the procedure discussed previously. The devolatilization appeared to be complete after about ten minutes. The temperature was maintained for a minimum of an additional five minutes to ensure uniformity in carrying out the devolatilization step. The char was held at that temperature and the steam flow was started. Steam flow rates of 0.5 to 200 mg/min were investigated in preliminary experiments to allow selection of a suitable rate. The flow rate, optimized at 1-6 mg/min, supplied steam at a rate sufficient to feed the reaction without showing signs of diffusion limitation and without causing condensation build-up on the cool parts of the balance. When excess steam flow caused condensation to collect on the unheated parts of the balance arm or on the electrical contacts of the balance or thermocouple, the instrument response became erratic.

When the optimum reaction conditions had been determined, all experiments were run in at least duplicate with excellent reproducibility, and reactivity parameters were averaged for use in calculating E_a and A . Since, in some experiments up to 10 % of the calculated weight of the fixed carbon did not react, 90% conversion was considered complete for interpreting data shown in Figure 1 and 2.

The reactions between uncatalyzed coal char and steam for each of the three coals when carried out at 750°C, showed that 90% conversion of char (fixed carbon) was most rapid in the Velva lignite (Figure 1). Ninety percent of Indian Head and Wyodak char conversion occurred at slower rates, with Wyodak being the slower as expected because of its higher rank (5).

Loading of 10 wt% K_2CO_3 catalyst gave the data plotted in Figure 2. Velva lignite chars achieved 90% conversion much more rapidly than any of the other chars tested.

The catalyst loading of 10 wt% Na_2CO_3 on Indian Head and Velva lignites was investigated and compared with the results from K_2CO_3 catalysis (Figures 3 and 4). The catalytic effect of 10 wt% Na_2CO_3 was nearly identical on a weight-to-weight basis to that of the K_2CO_3 up to 90% conversion for the Velva coal. It appeared to be slightly better than K_2CO_3 on a weight-to-weight basis for catalyzing the Indian Head char reaction. On a molar basis, however, K_2CO_3 was better for catalysis of both coal chars.

Uncatalyzed and K_2CO_3 -catalyzed coal char-steam reactions were also carried out at 700° and 800°C at the 10% catalyst loading. Mahajan, et. al., determined that a very useful parameter for correlating char reactivity data is the time needed to reach a fractional burn-off of 50% of the char (7). The reactivity parameter, K , was calculated from the conversion rate data at 700°, 750°, and 800°C based on weight of char sample reacted at 50% of fixed carbon versus time. Arrhenius plots of $\ln K_{0.5}$ versus $1/T$ were prepared (6), and E_a was calculated from the slope of the line, and A was determined from the Y-intercept (Figures 5, 6, and 7). These values are listed in Table III. For chars from Velva, Indian Head and Wyodak low-rank coals, the addition of K_2CO_3 decreased the apparent E_a by as much as 60% that of the uncatalyzed coal char. For equal wt% catalyst loading Na_2CO_3 was found to be at least as effective as K_2CO_3 in catalyzing the Velva and Indian Head char conversion. On a molar basis however the sodium catalyst would contain 1.30 times as many metal cations as the potassium catalyst when the coals are loaded with equal weights of the two catalysts. Although the Na_2CO_3 may not be as active atom for atom as K_2CO_3 , it was as effective in lowering the apparent energy of activation of the two lignites on a weight-for-weight basis and is much less expensive.

Table III. The Apparent Energies of Activation and Pre-exponential Factors Calculated from Arrhenius Plots at 0.5 of Fixed Carbon.

	Indian Head		Velva		Wyodak	
	E_a^*	A^{**}	E_a	A	E_a	A
As-received	28.8	1.78×10^6	29.8	4.11×10^6	31.8	7.67×10^6
K ₂ CO ₃ catalyzed	18.4	4.26×10^4	11.5	1.85×10^3	21.1	1.86×10^5
Na ₂ CO ₃ catalyzed	15.9	1.31×10^4	11.9	2.25×10^3	--	--

* Kcal/mole fixed carbon

** /hr

A few selected examples of apparent energies of activation from recent literature are shown in Table IV. Serageldin and Pan have suggested that the apparent energies of activation for the decomposition of coal change with operating conditions indicating that more than one mechanistic route is available (1). The data in Tables III and IV suggest that although coal rank is a factor in determining the reactivity of coal char and consequently E_a other factors such as time and temperature involved in char preparation, the quantity and type of mineral material in the coal, the gas content and composition as well as type and amount of catalyst have an effect on the value of E_a and A (1, 2, 8-10).

Table IV. Selected Literature Values of Apparent Energies of Activation.

Coal	Rank	Atmosphere	Catalyst Loading	Temp. Range (K)	E_a	Ref.
Illinois No.6	Bit	He/Steam	5% Na (as Na ₂ CO ₃)	873-1023	30.5	8
		He/Steam	10% Na (as Na ₂ CO ₃)	873-1023	24.5	8
Wyodak	Subbit	He/Steam	5% K (as K ₂ CO ₃)	873-973	44.8	1
		He/Steam	10% K (as K ₂ CO ₃)	873-973	39.1	1
Inland Mine	Subbit	N ₂		723-823	12.0	2
		N ₂		938-1223	16.1	2
		N ₂	4% Na (as Na ₂ CO ₃)	723-823	11.0	2
		N ₂	4% Na (as Na ₂ CO ₃)	938-1223	15.4	2
		N ₂	4% K (as K ₂ CO ₃)	723-823	11.5	2
		N ₂	4% K (as K ₂ CO ₃)	938-1223	13.6	2
PSOL-91	Lignite	N ₂ -Steam		1023-1163	42.1	5

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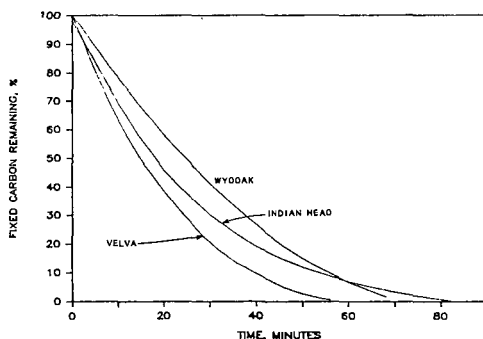


Figure 1. Uncatalyzed steam gasification - carbon conversion at 750°C.

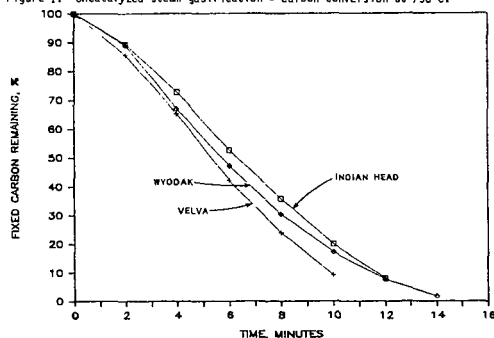


Figure 2. K_2CO_3 catalyzed steam gasification-carbon conversion at 750°C.

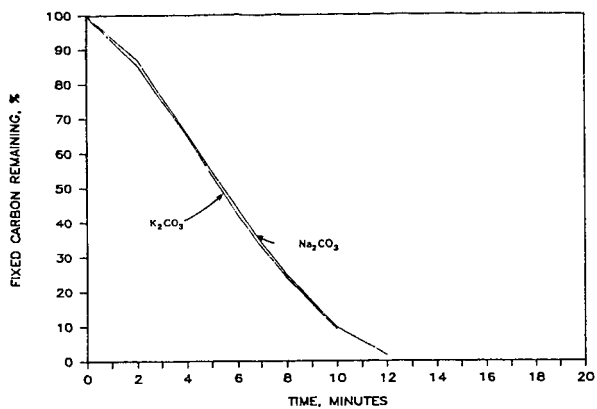


Figure 3. Catalysis of Velva lignite - steam gasification at 750°C.

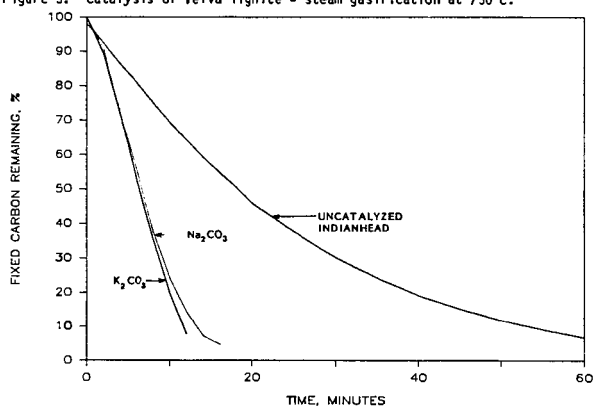


Figure 4. Catalysis of Indian Head lignite - steam gasification at 750°C.

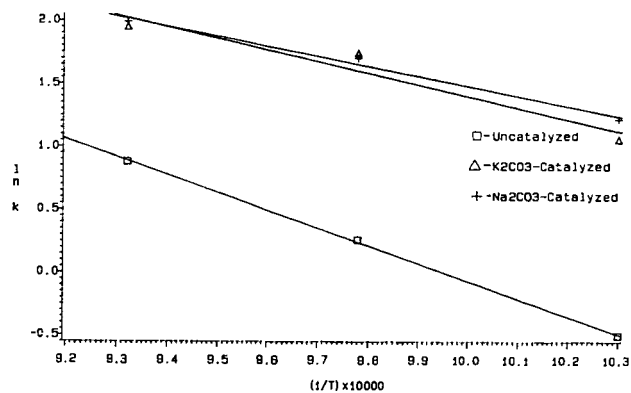


Figure 5. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Indian Head coal char with steam.

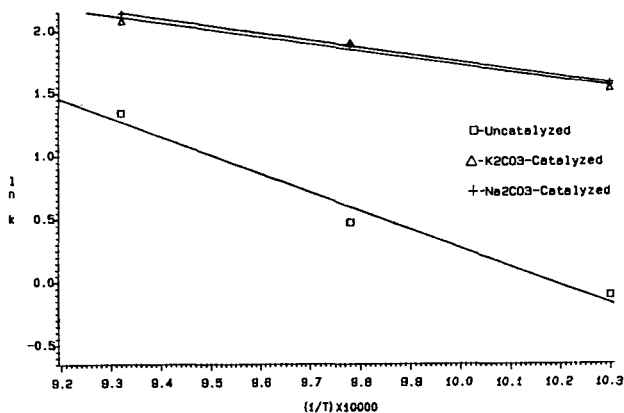


Figure 6. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Velve coal char with steam.

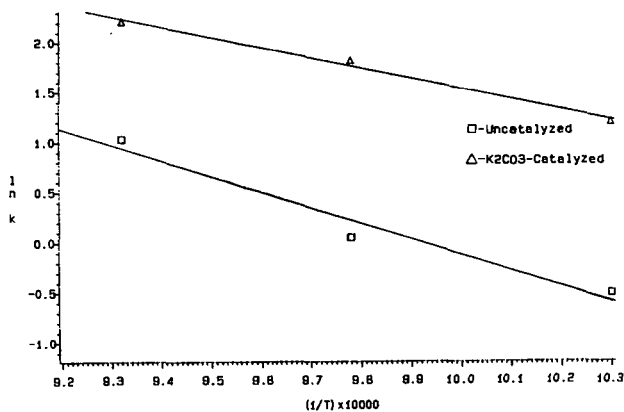


Figure 7. Arrhenius plots of the reactivities of catalyzed and uncatalyzed Wyodak coal char with steam.